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Convergent, Regioselective Synthesis of Tetrakisfulleroids from C_{60}

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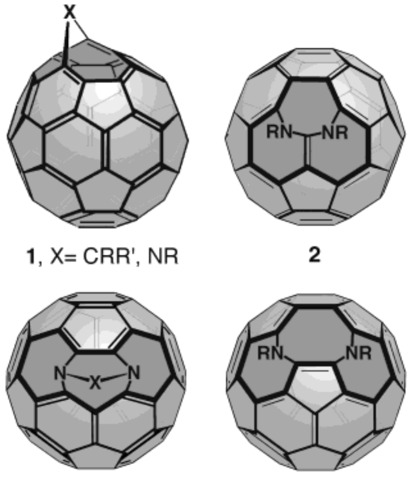
An efficient synthesis of the two diastereomeric tetrakisfulleroids **14a** and **14b** is described starting from the readily accessible *trans*-1 bis-Diels−Alder adduct **12**. The challenging issue of generating multiple bond scissions regiochemically within the fullerene framework, here as [5,6] open systems (fulleroids), is simplified into performing two separate regiocontrol phases. The initial bisadduct **12** can only undergo *syn* or *anti* photochemically promoted intramolecular tandem [4 + 4] and retro [2 + 2 + 2] rearrangements, giving the two isomers **14a** and **14b** in an unexpected 1:4 ratio. Interestingly, the UV−vis absorption spectra of these two isomers are quite different even though their local chromophore perturbations are distant from each other.

Introduction

One of the continuing challenges in fullerene chemistry lies in the control of regioselectivity of multiple functionalizations.[1] Thus far, most investigations have focused on additions to [6,6] ring junctions of C_{60} and other fullerene frameworks.[1,2] However, another important class of ring-opened [5,6] adducts (fulleroids, **1**) can be formed by initial [6,6] addition of diazo compounds[3] or azides[4] followed by a bond shift to a [5,6] ring junction under N_2 extrusion (Figure 1). Unlike in ring-closed [6,6] adducts, the number of π-electrons in fulleroids remains the same as in C_{60}, as one of the [5,6] single bonds is replaced by a homoconjugating bridge. This is reflected by the similar UV−vis absorption spectra of C_{60} and those of fulleroids.[3d]



1, X= CRR', NR **2**

3 **4**

FIGURE 1. General structure of [5,6] ring-opened fulleroids (**1**) and reported bisazafulleroids incorporating a cross-conjugated [11]annulene perimeter (**2**), a cross-conjugated [13]-annulene perimeter (**3**), and a conjugated [14]annulene perimeter (**4**).[5−7]

The selective multiple [5,6] fragmentation of the C_{60} core would provide an interesting variety of "homostructures" in which the arrangement and continuity of the fullerene π-system can be systematically adjusted while retaining the 60 π-electrons. This could prove useful in highly symmetrical hexakis- or dodecakis-homoconjugated systems whose reduction may lead to superconducting phases with T_c's higher than those of the C_{60} trianion salts as a result of the larger intermolecular spacing within the crystal lattice, as expected from the BCS theory of superconductivity. There are a few examples of bisfulleroids containing *N*-bridged 11-, 13-, or 14-membered rings formed by regioselective two-step azide additions to C_{60} (Figure 1).[5−7] However, compared to the degree of control achieved with regioselective functionalizations at [6,6] positions, further exploration of regiochemically defined multiple fulleroids has proven difficult because of the competitive formation of the corresponding ring-closed [6,6] adducts and the low symmetry of the fulleroid structures, which makes further additions regiochemically uncontrollable or the higher

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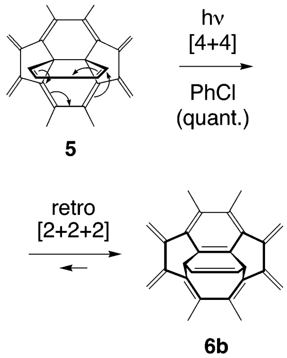

FIGURE 2. Photochemically promoted tandem rearrangement of cyclohexadiene-fused fullerenes (**5**) to bridged bisfulleroid **6b** incorporating a [12]annulene opening (*as*-indacene perimeter).[8]

fulleroid products practically uncharacterizable. Hence, controlled methods to form fulleroids are desirable.

We have reported that 1,2-(3′,5′-cyclohexadieno)buckminsterfullerene **5** undergoes a clean photochemically promoted *tandem* rearrangement to the bridged bisfulleroid **6b**.[8] This process presumably occurs via the initial [4 + 4] photoadduct **6a**,[9] followed by a thermal [2 + 2 + 2] cycloreversion to afford the bismethano[12]annulene structure **6b** (*as*-indacene perimeter, Figure 2). In this report, we describe the synthesis of a pair of "tetrakisfulleroids" **14a** and **14b** (Figure 4) in which a total of four [5,6] ring junctions are cleaved with a high degree of regiochemical control, constituting the first characterized "higher" fulleroids.

Results and Discussion

The one-pot bisfulleroid formation presents an advantage over stepwise approaches in that the required intermediate cyclohexadiene rings can be easily formed from a bis-Diels−Alder adduct.[10] The regioselectivity of multiple Diels−Alder cycloadditions at [6,6] ring junctions is intrinsically much easier to control as we have previously reported using a tether-templated approach.[2b] In this work, methyl phenylacetate groups were needed to facilitate separation and increase solubility of the final fulleroid products **14a** and **14b** (Figure 4). Starting from (4-ethynylphenyl)acetate, regioselective dichloroketene (Cl_3COCl, Zn−Cu couple) addition led to the corresponding dichlorocyclobutenone **7** (Figure 3). Dechlorination of **7** was achieved by using Zn/HOAc to give cyclobutenone **8**, which was then reduced to the unstable allylic alcohol **9** under the Luche conditions. The alcohol function in **9** was quickly converted to the desired precursor **11** by esterification with tolanediacetic acid dichloride (**10**).[2b] The 2-fold Diels−Alder cycloaddition of **11** to C_{60} was carried out under high dilution conditions (Figure 4). The *trans*-1 bisadduct **12** was isolated as a *rac* and *meso* diastereomeric mixture in 19% yield from the *trans*-2 diastereomeric mixture (34%) by flash chromatography (SiO_2, toluene to CH_2Cl_2). Subsequently, in the key transformation, removal of the tether in **12** (TsOH, *o*-dichlorobenzene, 130 °C) under visible light irradiation triggered a double cascade of [4 + 4] and retro[2 + 2 + 2] rearrangements at both poles of C_{60}, affording the two possible *anti* (**14a**) and *syn* (**14b**) tetrakisfulleroids. Column chromatography (SiO_2, CS_2/CH_2Cl_2 3:1 to 2:1) gave 10% of **14a** and 40% of **14b**. The unexpected preference for *syn* over *anti* product in this double photorearrangement must arise from the electronic configuration of the intermediate mono-rearranged product **13b**, even though the two addends are relatively remote from each other. The pericyclic nature of this mechanism is far from certain since it can be viewed as a double di-π-methane rearrangement and most certainly involves a triplet excited state.[9]

The two isomers **14a** and **14b** exhibit very similar peak patterns in their ^{1}H NMR spectra as a result of their similar C_2 and C_s symmetry. Nevertheless, they can be easily distinguished by their ^{13}C NMR spectra: For the C_2-symmetric *anti* isomer **14a**, 40 of the required 41 lines are observed, 30 of which are sp^2 carbon atoms within the fullerene framework (no half-intensity signals, Figure 5a), whereas *syn* isomer **14b** displays all of the expected 43 signals, 32 of which are sp^2 carbon atoms within the fullerene framework (Figure 5b). In particular, **14b** shows four signals in the 130−132 ppm region corresponding to the four sp^2 C-atoms highlighted in Figure 5b, all of which have half intensities of other fullerene signals, thus unambiguously establishing the C_s symmetric nature of this compound. The NMR assignment is also in good accord with the chromatographic behavior in which the *anti* isomer **14a** elutes slightly faster than its *syn* isomer **14b** as a result of the larger angular relationship between the two R_f-determining ester groups of **14b**.

The electronic configurations of isomers **14a** and **14b** differ only in the *anti* and *syn* alignments of the two bismethano[12]annulene subunits at the two poles of C_{60}. Although the total number of π-electrons is the same, the structural change is enough to give them different UV−vis absorption spectra (Figure 6). The color of **14b** in solution is purple and similar to that of C_{60} and simple fulleroids,[3,4,8] whereas **14a** has a yellowish brown color in dilute solutions. This difference can be attributed in part to a change in relative intensities of the two bands at 443 and 468 nm, being strong and weak, respectively, for *syn* isomer **14b**, and close to the reverse for *anti* isomer **14a**. The monotonic decrease of absorption from 480 to 700 nm for **14a** also contributes to its brown color.

In this efficient synthesis of **14a** and **14b**, the difficult issue of regiochemistry in multiple [5,6] open systems within the π-framework of C_{60} is simplified into performing two separate regiocontrol phases. Thus, by distinctly

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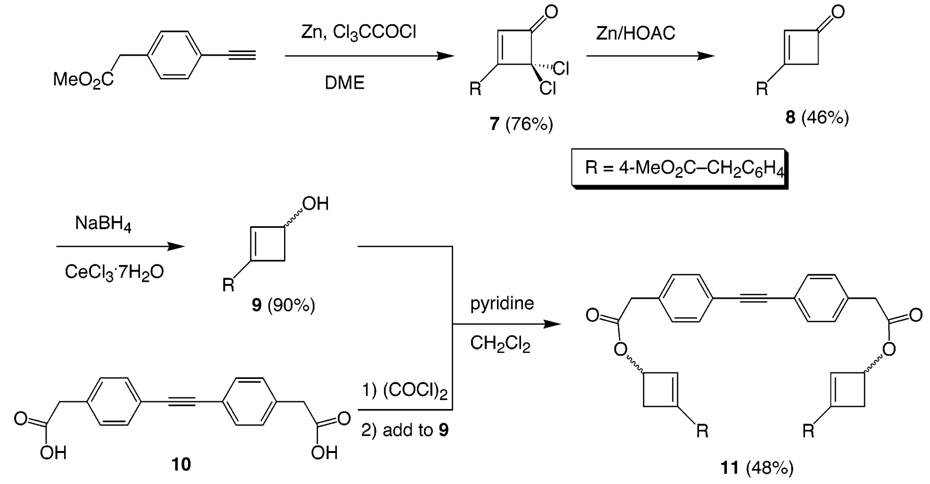

FIGURE 3. Synthesis of tethered biscyclobutenol ester **11**.

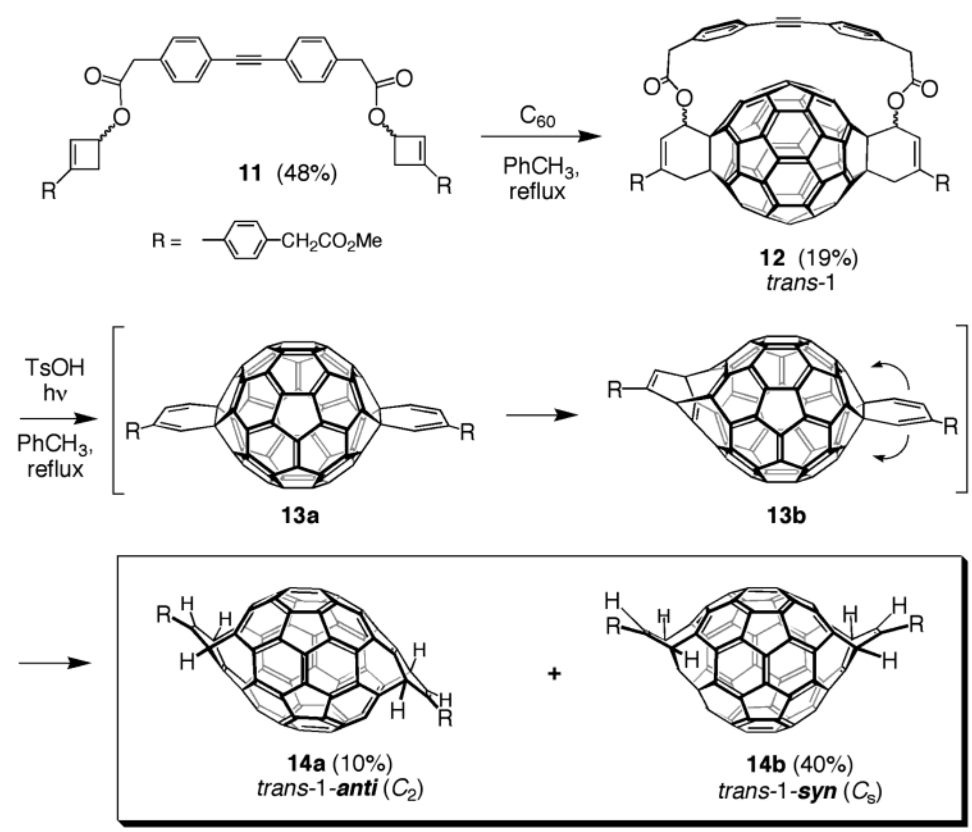

FIGURE 4. Regioselective synthesis of tetrakisfulleroids **14a** and **14b**.

taking advantage of both the regioselectivity of multiple [6,6] additions (Diels–Alder)[1,2,11] and the high efficiency of the photochemically promoted intramolecular tandem [4 + 4] and retro[2 + 2 + 2] rearrangement,[8–10] this combined strategy paves a general route toward a host of novel polyfulleroids in which $2n$ ($n = 1, 2, 3, 4, 5, 6$) number of [5,6] ring junctions can be selectively cleaved by rational design. This indicates exciting prospects, since some of the resulting polyfulleroids may exhibit both aesthetically appealing and electronically unique symmetrical structures that have no comparison with the [6,6] polyadducts of C_{60}. From another point of view, the incorporation of an increasingly higher number of the intrinsically antiaromatic [12]annulene substructures into the 60 π-electron framework could dramatically change their properties with certain patterns and degrees of addition, also depending on their degree of reduction.[12] A systematic synthetic and physical organic study along this direction is currently being pursued.

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(11) For other regioselective multiple Diels–Alder additions of C_{60}, see: (a) Kräutler, B.; Maynollo, J. *Angew. Chem.* **1995**, *107*, 69–70; *Angew. Chem., Int. Ed. Engl.* **1995**, *35*, 87–88. (b) Kräutler, B.; Müller, T.; Maynollo, J.; Gruber, K.; Kratky, C.; Ochsenbein, P.; Schwarzenbach, D.; Bürgi, H. B. *Angew. Chem.* **1996**, *108*, 1294–1296; *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 1204–1206. (c) Taki, M.; Sugita, S.; Nakamura, Y.; Kasashima, E.; Yashima, E.; Okamoto, Y.; Mishimura, J. *J. Am. Chem. Soc.* **1997**, *119*, 926–932. (d) Ishi-i, T.; Nakashima, K.; Shinkai, S. *J. Chem. Soc., Chem. Commun.* **1998**, 1725–1726.

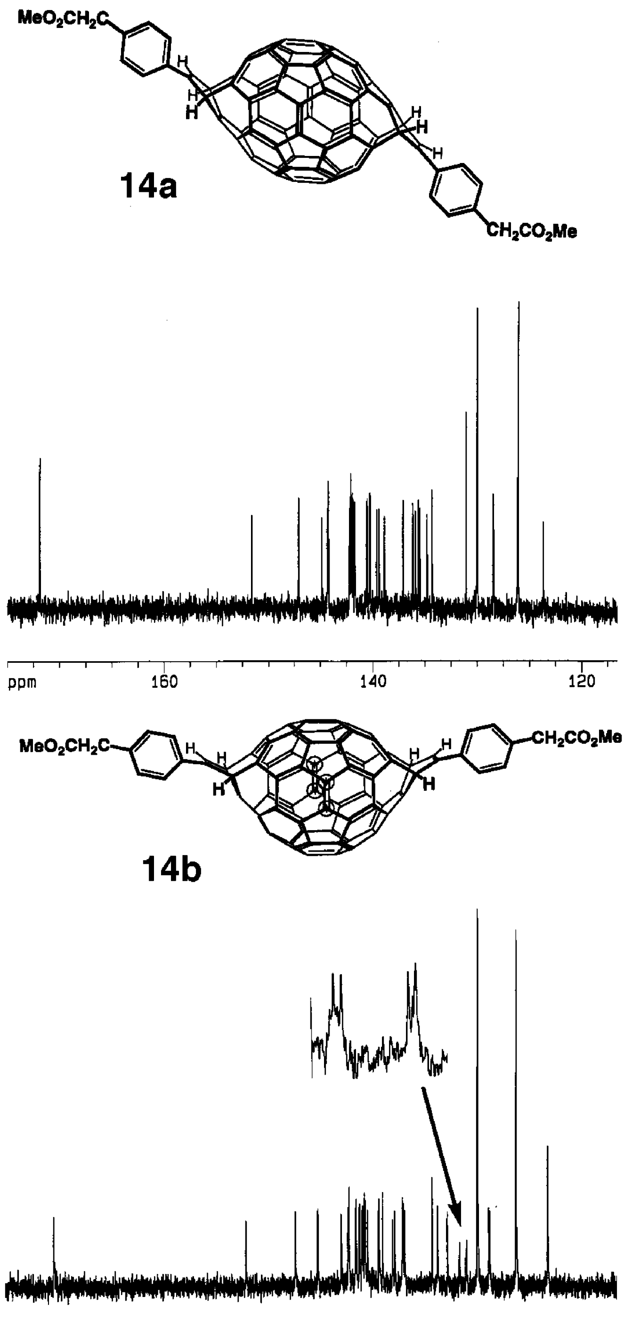

FIGURE 5. ^{13}C NMR spectra of compound **14a** ($C_2D_2Cl_4$) and **14b** (125 MHz, $CDCl_3/CS_2$ 1:4) in the sp^2 region.

Experimental Section

General Remarks. All reactions were performed under argon and, for $^1O_2$-sensitive compounds (all C_{60} derivatives containing the cyclohexeno or cyclohexadieno moieties), in absence of light. Me_4Si was used as the internal standard for ^{1}H NMR, and the deuterated solvent was used as a standard for ^{13}C NMR. ^{13}C NMR spectra were resolution enhanced with Gaussian broadening (LB = −1.0, GB = 0.3) to resolve most overlapping lines. The matrix used for FAB mass spectra was *m*-nitrobenzyl alcohol. Column chromatography was performed on silica gel 230−400 mesh (flash); thin-layer chromatography (TLC) was performed on glass plates coated with silica gel 60 F_{254} from E. Merck.

Materials. Pure C_{60} (99.8%) was obtained from two different sources.

Synthesis of 3-(4-(Carbomethoxymethyl)phenyl)-4,4-dichlorocyclobutenone (7). A 500-mL round-bottom flask was charged with 6.08 g (0.093 mol) of zinc−copper couple, 70 mL of dry ethyl ether, and 5.4 g (0.031 mol) of methyl 4-ethynyl-phenylacetate. A dropping funnel was charged with 6.92 mL (0.062 mol) of trichloroacetyl chloride in 20 mL of dry dimethoxyethane, and this solution was added dropwise to the stirred reaction mixture over 30 min. After stirring at room temperature for 30 h, the resulting brown mixture was filtered through a sintered-glass Buchner funnel with the help of 50 mL of ether. The filtrate was then washed successively with 40 mL each of ice-cold 0.5 M hydrochloric acid, 5% NaOH solution, and saturated sodium chloride solution, dried over magnesium sulfate, and then evaporated to dryness. Flash chromatography (SiO_2, CH_2Cl_2/hexane 1:1 to pure CH_2Cl_2) gave 6.74 g (76%) of **7** as a sticky liquid: ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 3.74 (s, 3H), 3.75 (s, 2H), 6.60 (s, 1H), 7.52 (d, J = 8.1 Hz, 2H), 7.89 (d, J = 8.1 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 41.20, 52.35, 89.61, 124.90, 130.07, 130.33, 130.57, 140.43, 170.81, 175.39, 178.86; FT-IR (KBr) ν (cm^{-1}) 2921.7 w, 2850.8 w, 1788.2 s, 1737.1 m, 1608.4 m, 1578.3 m, 1559.1 m, 1502.1 m, 1267.9 m, 1164.8 m, 1058.9 m, 840.1 m; HRMS (EI$^+$) calcd for $C_{13}H_{10}Cl_2O_3$ 284.0007, found 284.0006.

3-(4-(Carbomethoxymethyl)phenyl)cyclobutenone (8). A 500-mL flask was charged with 8.77 g (0.134 mol) of Zn dust, 20 mL of redistilled TMEDA, and 35 mL of absolute ethanol. The mixture was cooled in an ice bath, and then 7 mL of glacial acetic acid was added dropwise over 5 min. The reaction mixture was maintained at 0 °C while a solution of 6.56 g (0.023 mol) of **7** in 15 mL of absolute ethanol was added over 10 min via a dropping funnel. After 15 min, the ice bath was removed, and the mixture was stirred for another 10 min. The reaction mixture was then filtered with the help of 50 mL of ether. The filtrate was evaporated to remove most of the alcohol and then combined with 200 mL of ether. The combined solution was washed with 80 mL each of 1 M HCl, water, saturated sodium bicarbonate solution, and saturated sodium chloride solution, dried over magnesium sulfate, and evaporated to dryness. Flash chromatography (SiO_2, CH_2Cl_2/hexane 1:1 to pure CH_2Cl_2) gave 2.29 g (46%) of **8** as a white solid: ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 3.52 (s, 2H), 3.71 (s, 2H), 3.72 (s, 3H), 6.60 (s, 1H), 7.43 (d, J = 8.1 Hz, 2H), 7.59 (d, J = 8.1 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 41.08, 48.52, 52.22, 129.04, 129.67, 129.94, 130.28, 138.15, 170.46, 171.13, 187.25; FT-IR (KBr) ν (cm^{-1}) 2956.6 w, 2925.0 w, 1753.1 s, 1729.1 s, 1609.1 m, 1581.8 m, 1566.9 m, 1503.6 m, 1433.0 m, 1344.2 m, 1213.7 m, 1168.3 s, 1057.1 m, 816.9 m; HRMS (EI$^+$) calcd for $C_{13}H_{12}O_3$ 216.0786, found 216.0779.

3-(4-(Carbomethoxymethyl)phenyl)cyclobutenol (9). To a solution of 2.22 g (0.0103 mol) of **8** in 60 mL of MeOH was added 2.5 g of $CeCl_3{\cdot}7H_2O$. After cooling in an ice bath, 400 mg (0.0105 mol) of sodium borohydride was added in portions. After stirring at 0 °C for 10 min, the solvent was carefully evaporated at room temperature under reduced pressure. The crude product was then purified by flash chromatography (SiO_2, CH_2Cl_2 to CH_2Cl_2/ethyl acetate 2:1) to give 2.02 g (90%) of **9** as white unstable crystals: ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 1.85 (br s, 1H), 2.59 (dt, J = 12.9, 1.1 Hz, 1H), 3.17 (ddd, J = 12.9, 3.9, 0.7 Hz, 1H), 3.63 (s, 2H), 3.70 (s, 3H), 4.78 (d, J = 3.9 Hz, 1H), 6.32 (d, J = 0.7 Hz, 1H), 7.26 (d, J = 8.1 Hz, 2H), 7.35 (d, J = 8.1 Hz, 2H); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ (ppm) 40.43, 41.01, 52.11, 67.28, 125.63, 129.30, 129.33, 132.73, 134.40, 146.73, 171.79; FT-IR (KBr) ν (cm^{-1}) 3315.8 br s, 2953.8 w, 2921.4 w, 1740.6, 1430.8 m, 1242.0 s, 1112.7 m, 818.3 m; HRMS (EI$^+$) calcd for $C_{13}H_{14}O_3$ 218.0943, found 218.0949.

Diester 11 (Mixture of Diastereomers). To a stirred solution of 1.84 g (6.25 mmol) of tolanediacetic acid **10**^{2b} in 50

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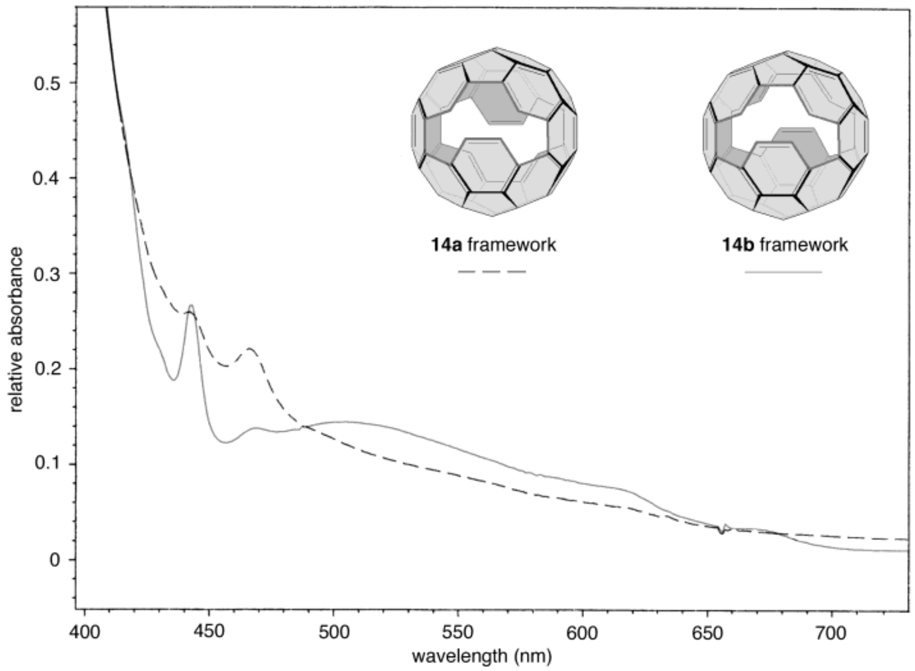

FIGURE 6. Schematic representation of the π-conjugated frameworks (bridging groups removed for clarity) and UV−vis spectra (1.0×10^{-4} M, CH_2Cl_2) of the isomeric tetrakisfulleroids **14a** (*anti*) and **14b** (*syn*).

mL of dry THF at 0 °C was added 8 mL (42 mmol) of oxalyl chloride. The flask was fitted with a drying tube, and the mixture was stirred at room temperature for 16 h. The solvent and the excess of oxalyl chloride were evaporated under reduced pressure to dryness, mixed with 50 mL of dry toluene, and evaporated to dryness again. The residue was further dried under high vacuum at 100 °C for 1 h and then cooled to 0 °C in an ice bath. A total of 2.0 g (9.2 mmol) of alcohol **9** in 50 mL of dry methylene chloride was added, followed by 2 mL of dry pyridine. After 1 h of stirring at 0 °C, the solvent was evaporated. The residue was purified by flash chromatography (SiO_2, CH_2Cl_2) to give 1.52 g (48%) of compound **11** as a white solid: ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 2.74 (d, $J = 13.1$ Hz, 2H), 3.21 (dd, $J = 13.1$, 3.9 Hz, 2H), 3.63 (s, 4H), 3.66 (s, 4H), 3.69 (s, 6H), 5.46 (d, $J = 3.9$ Hz, 2H), 6.30 (s, 2H), 7.27 (d, $J = 8.1$ Hz, 4H), 7.28 (d, $J = 8.1$ Hz, 4H), 7.35 (d, $J = 8.1$ Hz, 4H), 7.48 (d, $J = 8.1$ Hz, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 37.11, 41.02, 41.29, 52.12, 69.09, 89.23, 122.05, 125.35, 125.77, 129.30, 129.40, 131.75, 132.07, 134.14, 134.86, 148.13, 171.19, 171.67; FT-IR (KBr) ν (cm^{-1}) 2953.6 w, 1733.5 s, 1722.1 s, 1435.2 w, 1329.4 m, 1222.2 s, 1147.4 s, 807.0 m; HRMS (EI$^+$) calcd for $C_{44}H_{38}O_8$ 694.2566, found 694.2567.

Bisadduct 12 (Mixture of *rac/meso* Diastereomers). A solution of 750 mg (1.04 mmol) of C_{60} and 650 mg (0.935 mmol) of compound **11** in 1.4 L of toluene was degassed with a stream of argon for 20 min. The solution was then stirred at 110 °C for 24 h. The solvent was evaporated, and the residual mixture was purified by flash chromatography (SiO_2, toluene to CH_2Cl_2) to give 252 mg of **12** (19%, 23% based on recycled C_{60}) as a brown solid: ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm) 3.705 (s, 2H), 3.709 (s, 2H), 3.727 (s, 3H), 3.732 (s, 3H), 3.91 (m, 4H), 4.58 (br d, $J = 14.5$ Hz, 2H), 4.76 (br d, $J = 14.5$ Hz, 2H), 7.00−7.17 (m, 12H), 7.29 (d, $J = 3.1$ Hz, 1H), 7.32 (d, $J = 3.1$ Hz, 1H), 7.41 (d, $J = 8.2$ Hz, 2H), 7.42 (d, $J = 8.2$ Hz, 2H), 7.77 (d, $J = 8.2$ Hz, 2H), 7.78 (d, $J = 8.2$ Hz, 2H); FT-IR (KBr) ν (cm^{-1}) 2919.6 w, 2848.2 w, 1736.8 s, 1528.1 m, 1350.0 m, 1245.0 m, 1142.8 m; LRMS (FAB$^+$) calcd for $C_{104}H_{38}O_8$ 1415.46, found 1414.65.

The remaining brown fraction eluted with the same solvent afforded after evaporation 450 mg (34%) of a diastereomeric mixture of *trans*-2 bisadducts, as deduced from the UV−vis spectrum. This fraction was not investigated further for this work.

Tetrakisfulleroids 14a and 14b A solution of 42.5 mg (0.03 mmol) of **12** and 34.2 mg (0.18 mmol) of $TsOH{\cdot}H_2O$ in 20 mL of *o*-dichlorobenzene was degassed with a stream of argon for 15 min. The solution was then stirred at 130 °C under irradiation with a sun lamp for 1 h. After cooling to room temperature, the reaction mixture was directly submitted to flash chromatography (SiO_2, CS_2/CH_2Cl_2 3:1 to 2:1) to give 3.5 mg (10%) of **14a** (*anti*) as a brown solid and 13.3 mg (40%) of **14b** (*syn*) as a brown solid.

Data for 14a: ^{1}H NMR (500 MHz, $CDCl_2{-}CDCl_2$) δ (ppm) 3.76 (s, 10H), 6.84 (d, $J = 6.1$ Hz, 2H), 7.06 (s, 2H), 7.36 (d, $J = 6.1$ Hz, 2H), 7.48 (d, $J = 8.0$ Hz, 4H), 7.87 (d, $J = 8.0$ Hz, 4H); ^{13}C NMR (125.7 MHz, $CDCl_3$) δ (ppm) 40.64, 43.39, 45.71, 52.27, 123.65, 126.10, 128.39, 128.45, 129.99, 131.04*, 134.27, 134.76, 135.45, 135.58, 135.61, 135.89, 136.13, 137.05, 138.86, 139.36, 139.59, 140.22, 140.27, 140.51, 140.58, 141.69, 141.72, 141.87, 141.97, 142.02, 142.11, 142.12, 142.22, 144.22, 144.26, 144.34, 144.83, 147.06, 151.58, 171.89 (C_2 symmetry, 40 of the required 41 lines are observed. The asterisks indicate lines with double intensity due to accidental overlap); FT-IR (KBr) ν (cm^{-1}) 2919.7 w, 2848.2 w, 1737.2 s, 1433.6 w, 1255.7 m, 1154.0 s, 1014.0 w; LRMS (FAB$^+$) calcd for $C_{86}H_{24}O_4$ 1121.15, found 1120.96.

Data for 14b: ^{1}H NMR (500 MHz, $CS_2/CDCl_3$) δ (ppm) 3.64 (s, 4H), 3.76 (s, 6H), 6.77 (d, $J = 6.1$ Hz, 2H), 7.00 (s, 2H), 7.16 (d, $J = 6.1$ Hz, 2H), 7.36 (d, $J = 8.0$ Hz, 4H), 7.72 (d, $J = 8.0$ Hz, 4H); ^{13}C NMR (125.7 MHz, $CS_2/CDCl_3$) δ (ppm) 40.63, 43.30, 45.52, 51.47, 122.85, 125.92, 128.45, 128.54, 129.63, 130.67, 130.73, 131.32, 131.39, 132.54, 133.46, 133.99, 136.63, 136.77, 136.87, 137.59, 137.81, 138.76, 139.07, 139.14, 140.19, 140.40, 140.50, 140.52, 140.69, 140.75, 140.95, 141.03, 141.29, 141.38, 142.96, 142.01, 142.08, 142.72, 144.93 145.00, 147.10, 151.86, 171.37 (C_s symmetry, 43 of the required 43 lines are observed); FT-IR (KBr) ν (cm^{-1}) 2921.1 w, 2848.2 w, 1736.6 s, 1253.9 m, 1156.4 m, 1014.0w; LRMS (FAB$^+$) calcd for $C_{86}H_{24}O_4$ 1121.15, found 1122.06.

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